4

AD-A213 018

OFFICE OF NAVAL RESEARCH

Contract N00014-81-K-0605

Task No. NR 056-768

TECHNICAL REPORT NO. 18

Mechanisms in Reactive Ion Etching of Silicon Carbide Thin Films

by

W.-S. Pan and A.J. Steckl

Prepared for publication in Springer Proceedings in Physics,

Springer-Verlag

Nanoelectronics Laboratory
University of Cincinnati
Cincinnati, OH 45221-0030

1989

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) UC-TR 18	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION Nanoelectronics Laboratory University of Cincinnati 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research
6c. ADDRESS (City, State, and ZIP Code) 899 Rhodes Hall, ML 30 Cincinnati, OH 45221-0030	7b. ADDRESS (City, State, and ZIP Code) Chemistry Program Arlington, Virginia 22217
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Contract N 00014-81-K-0605
8c. ADDRESS (City, State, and ZIP Code) Chemistry Program Arlington, Virginia 22217	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO.: NR056-768 PROJECT NO.: TASK NO: WORK UNIT ACCESSION NO:

11. TITLE (Include Security Classification)

Mechanisms in Reactive Ion Etching of Silicon Carbide Thin Films

12. PERSONAL AUTHOR(S)

W.-S. Pan and A.J. Steckl

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Interim Technical	FROM ______ TO ______	1989	

16. SUPPLEMENTARY NOTATION

Prepared for publication in Springer Proceedings on Physics, Springer-Verlag

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	etching mechanisms, fluorinated gases, SiC, carbon blocking model

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The etching mechanisms for the reactive ion etching of SiC thin films were investigated using fluorinated gases, such as SF_6/O_2, CHF_3/O_2, $CBrF_3/O_2$. The major mechanisms involved are: (a) physical removal by sputtering due to ionized particles within the plamsa, (b) chemical reaction of active plamsa species with C and Si with the generation of volatile products. The self-induced DC Bias has been shown to have a very strong effect up to a certain cross-over value of around 300V. The effect is related to the rate-limiting removal of the C-rich surface layer. We have confirmed that the chemical reaction process proceeds by removal of Si through reactions with F species (to generate SiF_4) while C is removed by reactions with O_2 (to generate CO_x) only. No reaction between C and F was observed in the experimental results. A carbon blocking model is proposed to describe the etching profile under RIE mode.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. David L. Nelson	22b. TELEPHONE (Include Area Code) (202)696-4410 22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR — 83 APR edition may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

unclassified

Mechanisms in Reactive Ion Etching of Silicon Carbide Thin Films

W.-S. Pan* and A.J. Steckl**

* Intel Corporation, Santa Clara, CA 55052

** University of Cincinnati, Nanoelectronics Laboratory,
Department of Electrical and Computer Engineering, Cincinnati, OH 45221-0030

1. Abstract

The etching mechanisms for the reactive ion etching of SiC thin films were investigated using fluorinated gases, such as SF_6/O_2, CHF_3/O_2, $CBrF_3/O_2$. The major mechanisms involved are: (a) physical removal by sputtering due to ionized particles within the plasma, (b) chemical reaction of active plasma species with C and Si with the generation of volatile products. The self-induced DC Bias has been shown to have a very strong effect up to a certain cross-over value of around 300V. The effect is related to the rate-limiting removal of the C-rich surface layer. We have confirmed that the chemical reaction process proceeds by removal of Si through reactions with F species (to generate SiF_4) while C is removed by reactions with O_2 (to generate CO_x) only . No reaction between C and F was observed in the experimental results. A carbon blocking model is proposed to describe the etching profile under RIE mode.

2. Introduction

Plasma etching techniques have been employed to etch SiC in a number of fluorinated gases, such as CF_4/O_2, SF_6/He and Ar plasma [1]. The use of CF_4 [2, 3], CF_4/O_2 [1, 3, 4], NF_3 [5], SF_6 [6] plasmas to pattern SiC has been previously reported. These results concentrated on SiC etch rates under various conditions. A two step SiC etching model had been proposed [7]. In this paper, we report on the results of experiments designed to elaborate aspects of the SiC etching mechanisms. In particular, we have employed gases with high fluorine content (SF_6) and low fluorine content ($CBrF_3$ and CHF_3) in the RIE mode and we have analyzed the effect of plasma DC bias.

3. Experimental Procedure

SiC thin films were deposited by RF sputtering onto silicon substrates in a planar system. The film preparation and apparatus used in these experiments have been previously reported [1]. The etching

experiments were carried out in a parallel plate reactor equipped with a computer-controlled grating monochromator for measuring optical emission within the plasma [8]. The DC self-bias of the RF electrode was also monitored. The etching mechanism of each gas has been investigated by exposing large areas of SiC in the chamber to cause a loading effect. The surface coverage was from 10% to 40%. The changes of species density in the plasma caused by consuming large amount of reactants [9] were detected from optical emission spectra at various emission wavelengths, such as [F] (703nm) and [O] (77nm). Reaction by-products monitored at other wavelengths could also be formed in the gas phase by the process gases themselves, such as $CBrF_3$ and CHF_3 leading to [CO] (297nm) and [CF_2] (289nm). Therefore, a comparison spectrum was used to eliminate this possible effect from the experiments. Resulting measurements of carbon products were, therefore, considered to be contributed by the SiC only. The [CO_x] and [CF_x] intensity could be detected at many different wavelengths, such as 283nm, 297nm, 313nm for [CO], 290nm for [CO_2^+], 275nm, 262nm, 290nm for [CF_2], etc.

4. Results and Discussions

The pressure dependence of SiC, Si and SiO_2 etch rates in SF_6/O_2 plasma is shown in Figs. 1 and 2. It is important to note that as the DC bias increases with decreasing pressure the SiC etch rate monotonically increases until a bias of approximately 300V is reached. For higher values of DC bias, the etch rate is apparently no longer linked to the bias but rather depends on the concentration of reactants, namely oxygen and fluorine, in the plasma. The behavior of the Si etch rate, on the other hand, appears to be independent of the DC bias and only a function of the fluorine concentration. Similar SiC and Si characteristics are observed in $CBrF_3/O_2$ plasma. Based on these observations, we postulate two regimes for the bias dependence of the SiC etch rate. As shown in Fig. 3, in regime I, the etching of the SiC films is rate controlled by the DC bias. In region II, above a critical value of the bias, the etch rate becomes reaction-limited. Since the Si is readily etched by fluorine even at low bias levels, we conclude that it is the reaction between carbon in the SiC and oxygen in the plasma that controls the SiC etch rate and needs to be enhanced by the DC bias. This was confirmed by Auger studies of the SiC surface layers before and after reactive ion etching. A carbon-rich surface was found in all cases, with the amount of C decreasing with increasing O_2% in the plasma.

The RIE etching mechanisms for SiC in SF_6/O_2 plasmas were investigated by etching four 3" SiC-covered samples (40% coverage) and measuring the DC bias, [F] (703nm), [O] (777nm), [CF_2] (289nm) and [CO] (297nm) intensities during etching by SF_6/35%O_2 at 200W, 20sccm, 20mTorr. In Fig. 4 (a), the intensity of the comparison spectrum is shown displaying the differences between "no sample" plasma (positive part) case and SiC sample loaded plasma (negative part). The main reactants and products are marked. The data for [CO], [F] and [O] density versus etching time is shown in Fig. 4 (b), starting with the unloaded plasma (time <0), followed by the time period of etching the SiC film (0 ≤ time ≤ 3.5min) and finishing with etching of the Si substrate. The [CO] density was measured from the comparison spectra. Both [F] and [O] density decreased during the etching cycle. The [CO] density shows a clear relation to the etching process. No [CF_2] peak was found. Similar results were obtained for SF_6/90%O_2, $CBrF_3$/70%O_2 and CHF_3/90%O_2 etching of SiC.

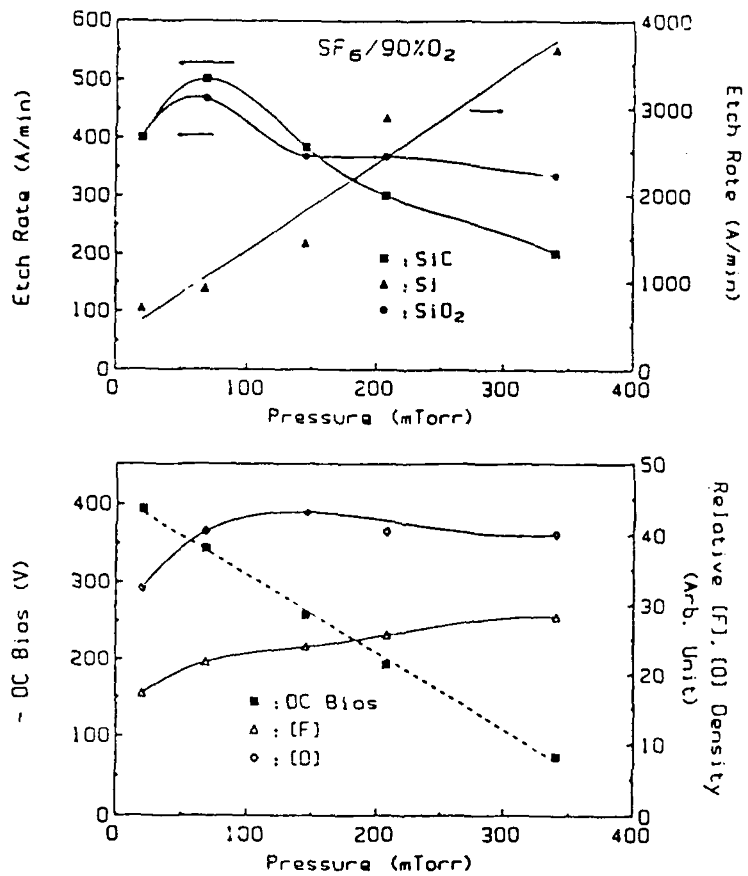

Fig. 1 RIE of SiC, Si and SiO_2 in $SF_6/90\%O_2$ mixtures as a function of pressure: (a) etch rates; (b) DC bias and plasma species densities

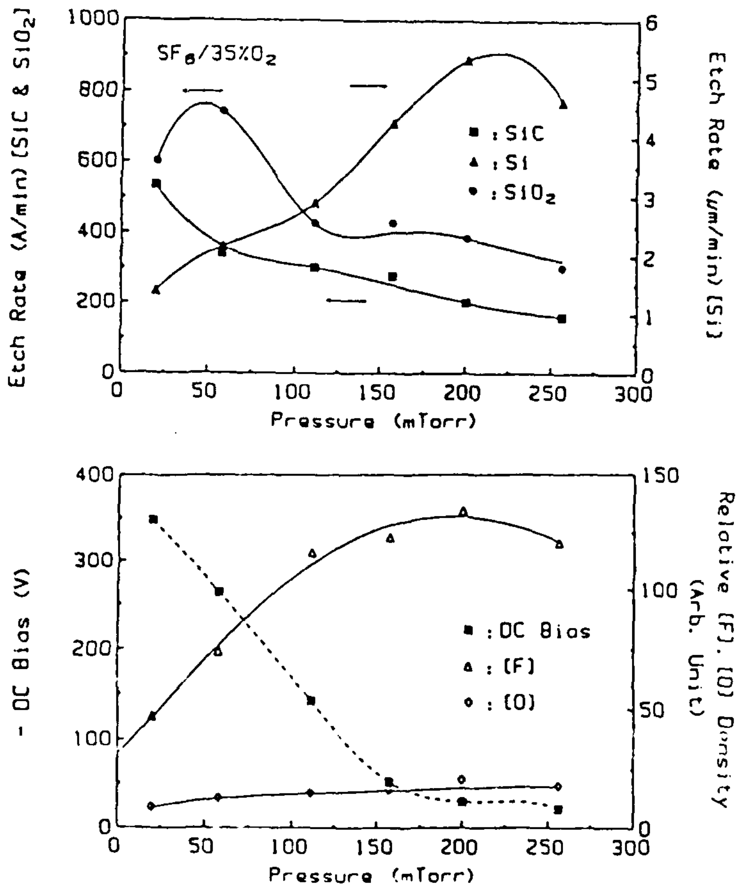

Fig. 2 RIE of SiC, Si and SiO_2 in $SF_6/35\%O_2$ mixtures as a function of pressure: (a) etch rates; (b) DC bias and plasma species densities

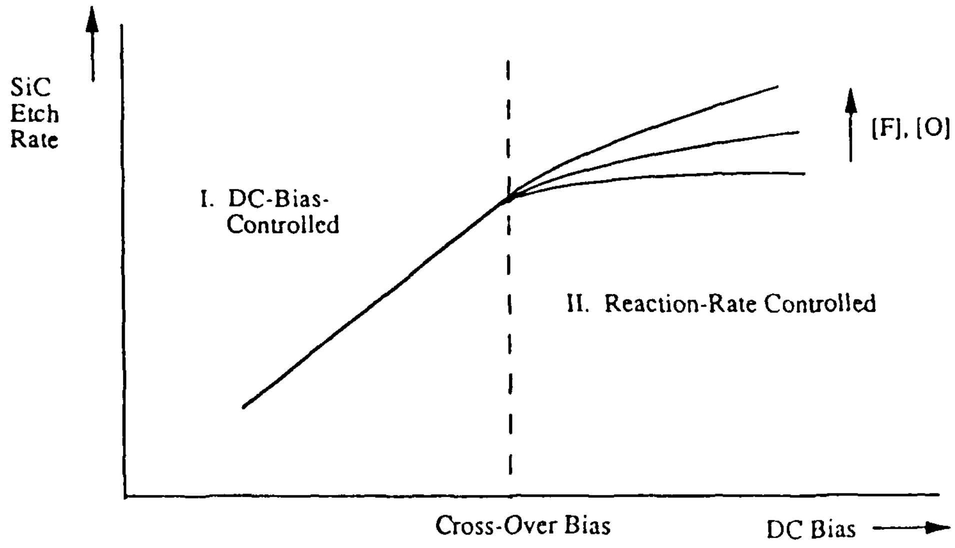

Fig. 3 Schematic of SiC etch rate dependence on plasma DC bias

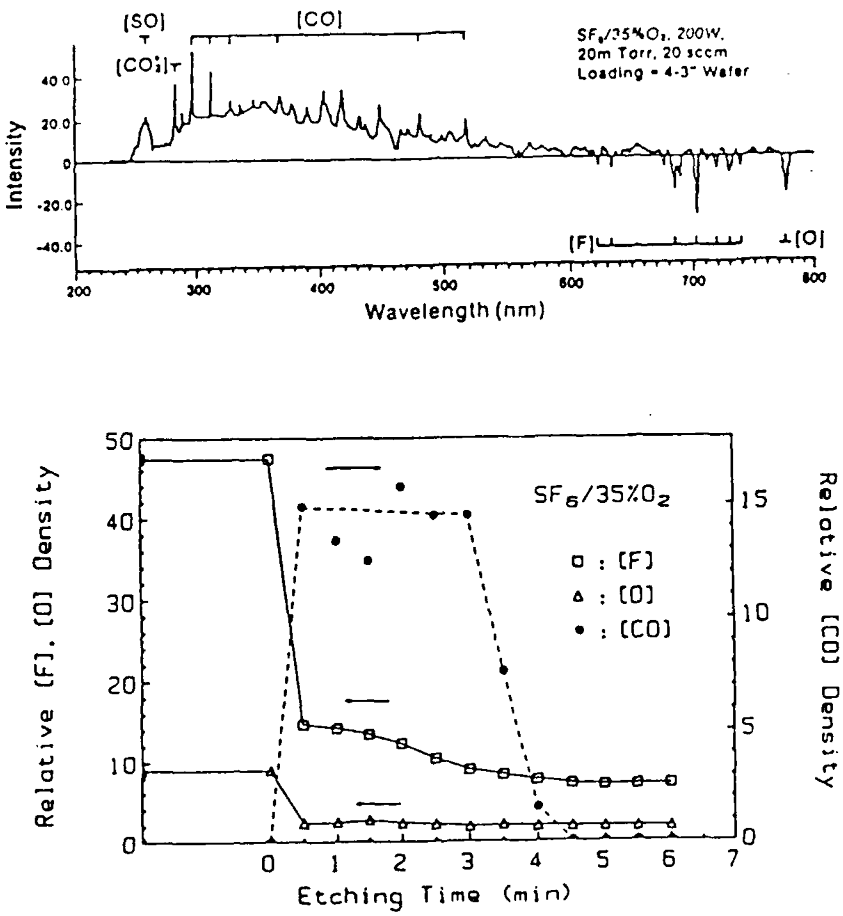

Fig. 4 Loading experiment of etching four 3" SiC wafers at $SF_6/35\%O_2$: (a) comparison spectrum; (b) relative [F], [O], [CO] density

To further investigate SiC etching phenomena, visual observation of the etching process was carried out through the quartz window of the chamber. For these experiments oxidized Si substrates were used since the SiO_2 presents a sharper color change from SiC (green) to SiO_2 (dark red). This color change

was used to recognize the end-point of the SiC etching experiments. The SiC film thickness at the wafer edge was 10% thinner than in the center region due to a sputtering effect during deposition, resulting in a "ring" effect where the SiO_2 layer is reached. The etching patterns obtained by using $SF_6/35\%O_2$, $SF_6/90\%O_2$, $CBrF_3/75\%O_2$ and $CHF_3/90\%O_2$ plasma at 200W, 20mTorr and 20sccm are shown schematically in Fig. 5. For the low concentration oxygen case, such as $SF_6/35\%O_2$, when a 3" SiC wafer was etched, the oxygen concentration was depleted along the direction of flow. Thus, the etching of SiC was dominated by the mass-transfer process and the etch rate of the wafer edge close to the gas inlet was faster than the edge close to the exhaust outlet (center). In the high oxygen concentration case, the reaction-limit will dominate the etching and because of the variation of SiC film thickness, the etching pattern was round and symmetric. The effect of the carbon-rich surface in SiC etching is shown to be the limiting step. The oxygen has a strong effect on the removal of this carbon layer and improves SiC etch rate. Fluorine was shown not to play a major role in removing carbon under these etching conditions.

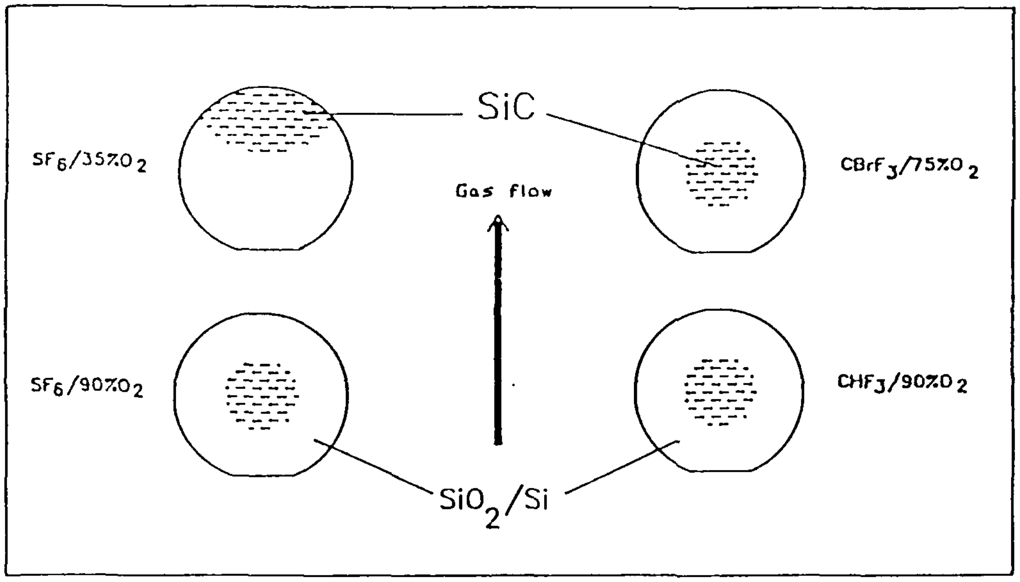

Fig. 5 SiC etching phenomena by different gases and composition of oxygen at 200W, 20sccm, 20mTorr in RIE mode

Based on the experimental results discussed above, we conclude that the etching of SiC in the reactive ion etching process consists of two basic mechanisms: physical removal and chemical reaction. For SiC and Si etching in fluorinated gases the most likely chemical reactions are given below:

$$Si + 4F \dashrightarrow SiF_4 \quad (1)$$

$$C + xO \dashrightarrow (CO, CO_2) \quad (2)$$

$$SiC + xF + yO \dashrightarrow SiF_4 + (CO, CO_2) . \quad (3)$$

In the reaction of (1), Si is removed mainly by reacting with fluorine to form volatile SiF_4 molecules. The required energy for this reaction is believed to be much lower than the energy needed for the oxygen - carbon reaction of (2). No carbon fluoride product was identified from the emission spectra, even in abundant fluorine concentration gases, such as the $SF_6/35\%O_2$ loading experiments. Hence, only

oxygen is considered in the carbon removal reaction (2) and the reaction between carbon and fluorine is suggested to occur at a very low rate. Therefore, in the etching of SiC, a two-step etching process, shown in (3), is considered to be an appropriate etching model, wherein silicon and carbon atoms are removed separately. Under most conditions, the Si etch rate is higher than that of SiC. This is due to comparatively higher removal rate of Si atoms than C atoms. As a result, a carbon-rich surface is formed on the SiC film during etching, becoming a potentially rate-limiting step under certain conditions. The C-rich surface has been verified by Auger electron spectroscopy (AES) and could be reduced by increasing oxygen concentration and DC bias.

A carbon blocking model shown Fig. 6 (a) is proposed to understand the physical etching mechanism in reactive ion etching of SiC. In general, surface damage and inhibitor mechanisms [11, 12] have been used to explain the anisotropic etching caused by ions in plasma etching. The result of ion bombardment caused by the plasma-induced DC bias on the electrode carrying the samples will cause a more directional etching and will remove surface inhibitors from the exposed region. In turn this will generate more etching sites where material can be removed by chemical reaction. However, ion bombardment is not effective at removing material from the sidewall (parallel to the ion direction). Therefore, a carbon-rich surface remains on the SiC sidewall reducing the lateral etching, thus resulting in a more highly anisotropic etching. The carbon layer was assumed to be the main type of inhibitor. In Fig. 5 (b), the carbon blocking layer is used to explain the etching phenomenon of the strong undercut situation of Si substrate [11]. The lower surface of the SiC layer was protected by the carbon-rich layer, preventing etching from the backside. The fact that neutral fluorine species available in ample concentrations did not result in SiC etching supports our carbon blocking model.

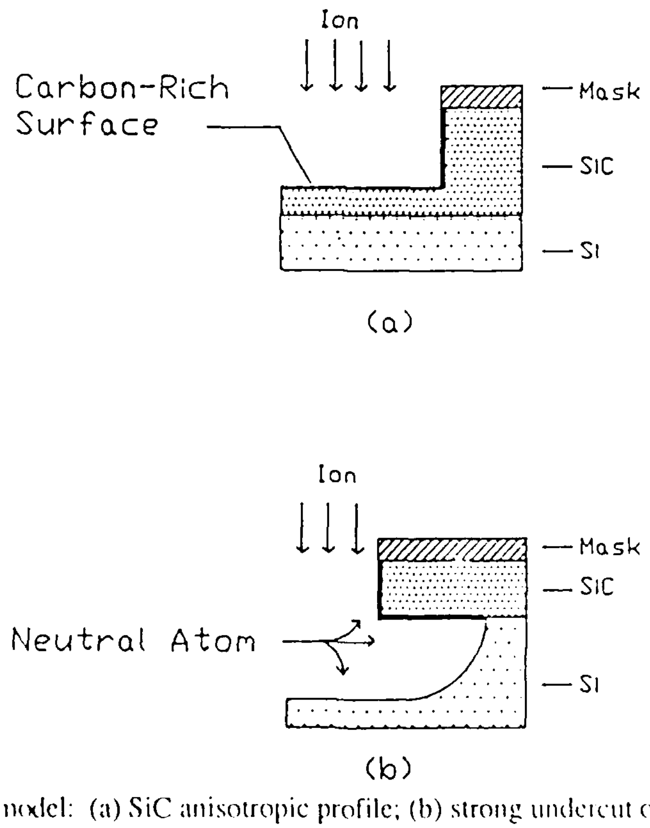

Fig. 6 Carbon-blocking model: (a) SiC anisotropic profile; (b) strong undercut of Si substrate situation

5. Summary

The SiC etch rate appears to be controlled by a combination of physical (DC bias) and chemical (fluorine and oxygen density) mechanisms. A cross-over DC bias, -300V, appears to separate the regions of chemical and physical rate-limiting domination of the SiC etch rate. Chemical reaction model and carbon-blocking model have been established and agree qualitatively with experimental results.

6. Acknowledgement

The authors would like to acknowledge partial support for this work from the Office of Naval Research, under ONR contract NO. N00014-81-K-0605.

7. References

1. J. Sugiura, W-J. Lu, K.C. Cadien and A.J. Steckl, J. Vac. Sci. Tech., Vol. B4, 349 (Jan./Feb. 1986).

2. S. Krongelb, IBM Technical Disclosure Bulletin, Vol. 23, No. 2, 828 (July, 1980).

3. John W. Palmour, R.F. Davis, P. Astell-Burt and P. Blackborow, Mat. Res. Soc. Symp. Proc., Vol. 76, 185 (1987).

4. S. Dohmae, K. Shibahara, S. Nishino and H. Matsunami, Jap. J. Appl. Phys., Vol. 24, No. 11, L873 (Nov. 1985).

5. J.W. Palmour, R.F. Davis, T.M. Wallett and K.B. Bhasin, J. Vac. Sci. Technol. A, Vol. 4, No. 3, 590 (May/Jun. 1986).

6. G. Kelner, S.C. Binari and P.H. Klein, J. Electrochem. Soc., Vol. 134, No. 1, 253 (Jan. 1987).

7. W-S. Pan and A.J. Steckl, Mat. Res. Soc. Symp. Proc., Vol. 76, 157 (1987).

8. R.W.B. Pearse and A.G. Gaydon, "The Identification of Molecular Spectra," London (1950).

9. C.J. Mogab, J. Electrochem. Soc., 124, 1262 (1977).

10. W-S. Pan, Ph.D. Thesis, Rensselaer Polytechnic Institute, Troy, NY, Aug. 1988.

11. H.F. Winters and J.W. Coburn, Appl. Phys. Lett., 34(1), 70 (1979).

12. C.J. Mogab and H.J. Levinstein, J. Vac. Sci. Technol., 17(3), 721 (1980).